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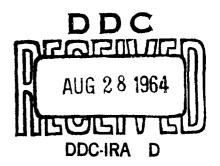
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THE DIELECTRIC CONSTANTS OF ARGON, CARBON DIOXIDE,
NITROGEN, AND OXYGEN DETERMINED AT AN AUDIO
FREQUENCY

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THE DIELECTRIC CONSTANTS OF ARGON, CARBON DIOXIDE, NITROGEN, AND OXYGEN DETERMINED AT AN AUDIO FREQUENCY*

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ABSTRACT

Values of the relative permittivities, or dielectric constants, of four gases have been measured at an audio frequency of 1592 c.p.s. with an accuracy comparable to that obtained in the microwave or optical regions. The method is based on the characteristics of the computable cross-capacitance configuration which permit the accurate calculation of changes of capacitance due to variation of dimensions with gas pressure, aided by the improved capacitance measurements now available. The results obtained are as follows:

Gas	$(\kappa' - 1)10^6(20^\circ \text{ C}, 1 \text{ atm})$	(κ' - 1)106(0° C, 1 atm)
Argon	516.59 ± 0.2	554.54 ± 0.2
Carbon dioxide	921.62 ± 0.3	990.55 ± 0.3
Nitrogen	547.40 ± 0.2	587.58 ± 0.2
Oxygen	494.31 ± 0.2	530.61 ± 0.2

These results verify the extrapolation of the optical refractivity data to zero frequency for argon, nitrogen, and oxygen in which the atomic polarization constant is zero. On the other hand carbon dioxide, which has a strong infrared vibration-rotation spectrum, may not be extrapolated from optical data, but must be measured at the lower frequencies.

The measured values of these reference gases may be used to calibrate other permittivity apparatus and so extend the data on other substances.

INTRODUCTION

Values of the dielectric constants of gases have been of interest to both physicists and chemists over a long period of years, and latterly the fields of communication and distance measuring have given new impetus to the need for accurate, reliable values. Many experimental methods for making such measurements have been devised, although generally the dielectric constant of a gas is determined from a change in capacitance of a capacitor charged with gas at various pressures, either measured directly or by a change in resonant frequency.

Despite the improvements in accuracy of capacitance measurements, and the vastly increased precision of measuring capacitance changes, the change of capacitance with change of pressure $\partial c/\partial p$ due to the variation of physical dimensions has always been troublesome and has tended to set a limit to the accuracy of the determination of dielectric constants of gases. Except for certain measurements, particularly those of Essen and Froome (1951) and Essen (1953), greater reliability seems to have been placed on the optical measurements of refractive index and dispersion. If it is assumed that

7

^{*}Issued as N.R.C. No. 7999.

(1)
$$\kappa' \kappa'_m = \frac{\epsilon' \mu'}{\epsilon_0 \mu_0} = \eta_\infty^2,$$

where the magnitude of the relative permeability κ'_m is unity except for oxygen and air, the relative permittivity κ' may be derived from the refractive index for infinite wavelength η_{∞} obtained from the optical dispersion formulae. This extrapolation procedure unfortunately disregards the contribution of the atomic polarization α_a to the dielectric constant. The atomic polarization, however, may not be neglected, particularly for those molecules which exhibit strong infrared vibration—rotation spectra.

In the last decade, developments of capacitance-measuring techniques have not only increased the absolute accuracy of measurement by more than an order of magnitude (McGregor et al. 1958; Dunn 1964) but have also improved the precision of measuring small capacitance changes by several orders of magnitude (Thompson 1958). Important as these advances are to the problem of measuring dielectric constants of gases, little advance could be made without the additional advantages derived from the computable cross capacitor (Thompson and Lampard 1956).

One important advantage is that the capacitance per unit length of a cross capacitor in the form of cylindrical bars has been shown (Lampard 1957) to be unaffected by a symmetrical change in radial dimensions of the bars. Hence it is only necessary to consider the variation of length of a uniform bar with change in ambient pressure in order to determine the value of $\partial c/\partial p$ for such a configuration. This is a straightforward calculation (Condon and Odishaw 1958), which leads to

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(2)
$$\frac{1}{c}\frac{\partial c}{\partial p}\Delta p = \frac{\Delta l}{l} = \frac{\Delta p}{E}(1-2\sigma),$$

where E= Young's modulus, $\sigma=$ Poisson's ratio, and $\Delta p=$ pressure change. Thus a capacitance configuration now exists in which the variation $(1/c)\partial c/\partial p$ may be computed with reliability, thereby opening the way to greater use of the increased accuracy and precision now available for capacitance measurements. In addition, in the cross-capacitance configuration there is no unwanted supporting solid dielectric in the active field of the capacitor. A third advantage is that the possible contamination of the electrode surfaces by thin films of unknown permittivity has a negligible effect on the measured capacitance (Lampard 1957; Lampard and Cutkosky 1960).

The dielectric constants of four gases—argon, carbon dioxide, nitrogen, and oxygen—have been measured at an operating frequency of 1592 c.p.s., with the same computable cross capacitor which was used (Dunn 1964) to define the unit of capacitance in the National Research Council. The results verify the extrapolation of the optical-refractivity data to zero frequency for argon, nitrogen, and oxygen, but not for carbon dioxide. They also indicate the high degree of reliability attainable by this method, which in turn may be used to extend the data on other reference gases.

THEORY

None of the four gases is a perfect gas, and Berthelot's (1907) equation of state was chosen as being the most generally useful expression in the region of 20° C and pressures up to two atmospheres absolute, that is

(3)
$$pV = \frac{m}{M}RT \left[1 + \frac{9}{128} \frac{T_c}{\rho_c} \frac{p}{T} \left(1 - 6T_c^2/T^2 \right) \right],$$

where T_e and p_e are the critical temperature and pressure respectively.

The Clausius-Mosotti equation (Condon and Odishaw 1958) relating the molar polarization II to the total polarizability α and to the relative permittivity κ' is

(4)
$$\Pi = \frac{N_0 \alpha}{3\epsilon_0} = \frac{\kappa' - 1}{\kappa' + 2} \frac{M}{\rho}$$

from which

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$$(4a) \qquad \qquad \kappa' - 1 = (\kappa' + 2) \prod \rho / M.$$

Equations (3) and (4) may be combined by remembering that

$$\frac{\rho}{M} = \frac{m}{V} / M = \frac{m}{M} \cdot \frac{1}{V},$$

which leads to

(5)
$$\frac{\rho}{M} = \frac{1}{R} \frac{p}{T} \left[1 + \frac{9}{128} \frac{T_c}{p_c} \frac{p}{T} \left(1 - 6T_c^2 / T^2 \right) \right]^{-1}$$

and hence

(6)
$$(\kappa' - 1)_{t,p} = \frac{(\kappa' + 2)\Pi}{R} \cdot \frac{p}{T} \left[1 + \frac{9}{128} \frac{T_c}{p_c} \frac{p}{T} \left(1 - 6T_c^2 / T^2 \right) \right]^{-1},$$

(7)
$$(\kappa' - 1)_{20^{\circ}, 1 \text{ atm}} = \frac{(\kappa' + 2)\Pi}{R} \cdot \frac{1 \text{ atm}}{293.16} \left[1 + \frac{9}{128} \frac{T_{c}}{\rho_{c}} \frac{1 \text{ atm}}{293.16} \times (1 - 6T_{c}^{2}/293.16^{2}) \right]^{-1}.$$

By neglecting the variation of $\kappa' + 2$ with temperature and pressure, the ratio $Q_{t,p}$ of electric susceptibilities becomes

(8)
$$Q_{t,p} = \frac{(\kappa' - 1)_{t,p}}{(\kappa' - 1)_{20^{\circ}, 1 \text{ atm}}}$$

$$= \frac{p}{1 \text{ atm}} \cdot \frac{293.16}{T} \frac{\left[1 + \frac{9}{128} \frac{T_{c}}{p_{c}} \cdot \frac{1 \text{ atm}}{293.16} (1 - 6T_{c}^{2}/293.16^{2})\right]}{\left[1 + \frac{9}{128} \frac{T_{c}}{p_{c}} \cdot \frac{p}{T} (1 - 6T_{c}^{2}/T^{2})\right]}$$

and

(9)
$$(\kappa')_{t,p} = 1 + (\kappa' - 1)_{t,p}$$

$$= 1 + (\kappa' - 1)_{20^{\circ}, 1 \text{ atm}} \cdot Q_{t,p}.$$

The expressions used for evaluating the ratio $Q_{t,p}$ for the four gases are listed in Table I, along with the critical data.

TABLE I Conversion data

$Gas \qquad T_{c} (^{\circ}K) \qquad p_{o}(atm)$ $Argon \qquad 151.2 \qquad 48$ $Carbon \ dioxide \qquad 304.3 \qquad 73.0$ $Nitrogen \qquad 126.1 \qquad 33.5$ $Oxygen \qquad 154.4 \qquad 49.7$ $(Q_{t,p})_{A} = \frac{p}{760.34} \frac{1 + 0.591p \times 10^{-6}[1 - 0.0160(t - 20)]}{[1 + 0.003411(t - 20)]}$ $(Q_{t,p})_{CO_{2}} = \frac{p}{764.15} \frac{1 + 7.183p \times 10^{-6}[1 - 0.0653(t - 20)]}{[1 + 0.003411(t - 20)]}$ $(Q_{t,p})_{N_{2}} = \frac{p}{760.08} \frac{1 + 0.130p \times 10^{-6}[1 - 0.0378(t - 20)]}{[1 + 0.003411(t - 20)]}$ $(Q_{t,p})_{O_{2}} = \frac{p}{760.38} \frac{1 + 0.651p \times 10^{-6}[1 - 0.0154(t - 20)]}{[1 + 0.003411(t - 20)]}$ $(\kappa' - 1)_{t,p} = Q_{t,p} \cdot (\kappa' - 1)_{20^{\circ},1 \text{ atm}}$ $Q_{0^{\circ},1 \text{ atm}} = \frac{(\kappa' - 1)_{0^{\circ},1 \text{ atm}}}{(\kappa' - 1)_{20^{\circ},1 \text{ atm}}} = 1.07347 \text{ A}$ $= 1.07479 \text{ CO}_{2}$ $= 1.07348 \text{ O}_{2}$ $= 1.07348 \text{ O}_{2}$ $= 1.07322 \text{ perfect gas}$			
Carbon dioxide Nitrogen 126.1 33.5 Nitrogen 126.1 33.5 Oxygen 154.4 49.7 $(Q_{t,p})_{A} = \frac{p}{760.34} \frac{1 + 0.591p \times 10^{-6}[1 - 0.0160(t - 20)]}{[1 + 0.003411(t - 20)]}$ $(Q_{t,p})_{CO_2} = \frac{p}{764.15} \frac{1 + 7.183p \times 10^{-6}[1 - 0.0653(t - 20)]}{[1 + 0.003411(t - 20)]}$ $(Q_{t,p})_{N_2} = \frac{p}{760.08} \frac{1 + 0.130p \times 10^{-6}[1 - 0.0378(t - 20)]}{[1 + 0.003411(t - 20)]}$ $(Q_{t,p})_{O_2} = \frac{p}{760.38} \frac{1 + 0.651p \times 10^{-6}[1 - 0.0154(t - 20)]}{[1 + 0.003411(t - 20)]}$ $(\kappa' - 1)_{t,p} = Q_{t,p} \cdot (\kappa' - 1)_{20^{\circ}, 1 \text{ atm}}$ $Q_{0^{\circ}, 1 \text{ atm}} = \frac{(\kappa' - 1)_{0^{\circ}, 1 \text{ atm}}}{(\kappa' - 1)_{20^{\circ}, 1 \text{ atm}}} = 1.07347 \text{ A}$ $= 1.07479 \text{ CO}_2$ $= 1.07340 \text{ N}_2$ $= 1.07348 \text{ O}_2$	Gas	T _c (°K)	p₀(atm)
$(Q_{t,p})_{\text{CO}_2} = \frac{p}{764.15} \frac{1 + 7.183p \times 10^{-6}[1 - 0.0653(t - 20)]}{[1 + 0.003411(t - 20)]}$ $(Q_{t,p})_{\text{N}_2} = \frac{p}{760.08} \frac{1 + 0.130p \times 10^{-6}[1 - 0.0378(t - 20)]}{[1 + 0.003411(t - 20)]}$ $(Q_{t,p})_{\text{O}_2} = \frac{p}{760.38} \frac{1 + 0.651p \times 10^{-6}[1 - 0.0154(t - 20)]}{[1 + 0.003411(t - 20)]}$ $(\kappa' - 1)_{t,p} = Q_{t,p} \cdot (\kappa' - 1)_{20^{\circ},1 \text{ atm}}$ $Q_{0^{\circ},1 \text{ atm}} = \frac{(\kappa' - 1)_{0^{\circ},1 \text{ atm}}}{(\kappa' - 1)_{20^{\circ},1 \text{ atm}}} = 1.07347 \text{ A}$ $= 1.07479 \text{ CO}_2$ $= 1.07340 \text{ N}_2$ $= 1.07348 \text{ O}_2$	Carbon dioxi Nitrogen	de 304.3 126.1	73.0 33.5
$(Q_{l,p})_{N_2} = \frac{p}{760.08} \frac{1 + 0.130p \times 10^{-6}[1 - 0.0378(t - 20)]}{[1 + 0.003411(t - 20)]}$ $(Q_{l,p})_{O_2} = \frac{p}{760.38} \frac{1 + 0.651p \times 10^{-6}[1 - 0.0154(t - 20)]}{[1 + 0.003411(t - 20)]}$ $(\kappa' - 1)_{l,p} = Q_{l,p} \cdot (\kappa' - 1)_{20^{\circ}, 1 \text{ atm}}$ $Q_{0^{\circ}, 1 \text{ atm}} = \frac{(\kappa' - 1)_{0^{\circ}, 1 \text{ atm}}}{(\kappa' - 1)_{20^{\circ}, 1 \text{ atm}}} = 1.07347 \text{ A}$ $= 1.07479 \text{ CO}_2$ $= 1.07340 \text{ N}_2$ $= 1.07348 \text{ O}_2$	$(Q_{t,p})_{A} = \frac{p}{760.34} \frac{1}{1}$	$\frac{+\ 0.591p \times 10^{-6}[1}{[1+0.0034]}$	$\frac{-0.0160(t-20)]}{11(t-20)]}$
$(Q_{t,p})_{O_2} = \frac{p}{760.38} \frac{1 + 0.651p \times 10^{-6}[1 - 0.0154(t - 20)]}{[1 + 0.003411(t - 20)]}$ $(\kappa' - 1)_{t,p} = Q_{t,p} \cdot (\kappa' - 1)_{20^{\circ},1 \text{ atm}}$ $Q_{0^{\circ},1 \text{ atm}} = \frac{(\kappa' - 1)_{0^{\circ},1 \text{ atm}}}{(\kappa' - 1)_{20^{\circ},1 \text{ atm}}} = 1.07347 \text{ A}$ $= 1.07479 \text{ CO}_2$ $= 1.07340 \text{ N}_2$ $= 1.07348 \text{ O}_2$	$(Q_{l,p})_{\text{CO}_2} = \frac{p}{764.15} \frac{1}{1}$	$+7.183p \times 10^{-6}[1$ [1 + 0.0034]	$\frac{-0.0653(t-20)]}{11(t-20)]}$
$Q_{0^{\circ},1 \text{ atm}} = \frac{(\kappa' - 1)_{0^{\circ},1 \text{ atm}}}{(\kappa' - 1)_{20^{\circ},1 \text{ atm}}} = 1.07347 \text{ A}$ $= \frac{(\kappa' - 1)_{20^{\circ},1 \text{ atm}}}{(\kappa' - 1)_{20^{\circ},1 \text{ atm}}} = 1.07479 \text{ CO}_{2}$ $= 1.07340 \text{ N}_{2}$ $= 1.07348 \text{ O}_{2}$	$(Q_{l,p})_{N_2} = \frac{p}{760.08} \frac{1}{1}$	$\frac{+0.130p \times 10^{-6}[1}{[1+0.0034]}$	$\frac{-0.0378(t-20)]}{11(t-20)]}$
$Q_{0^{\circ},1 \text{ atm}} = \frac{(\kappa' - 1)_{0^{\circ},1 \text{ atm}}}{(\kappa' - 1)_{20^{\circ},1 \text{ atm}}} = 1.07347 \text{ A}$ $= 1.07479 \text{ CO}_{2}$ $= 1.07340 \text{ N}_{2}$ $= 1.07348 \text{ O}_{2}$	$(Q_{i,p})_{\mathcal{O}_2} = \frac{p}{760.38} \frac{1}{}$	$\frac{+0.651p \times 10^{-6}[1]}{[1+0.0034]}$	$\frac{-0.0154(t-20)]}{11(t-20)]}$
= 1.07022 periect gas		°,1 atm = 1.07347 / = 1.07479 (= 1.07348 (= 1.07348)	A CO ₂ N ₂ O ₂
		_ 1.07022	pericet gas

The capacitance at temperature t and pressure p of a capacitor filled with a gas of relative permittivity κ' is given by

(10)
$$C_{t,p} = \kappa'_{t,p} \left(C_{t,0} + \frac{\partial C_{t,0}}{\partial p} \Delta p \right),$$

from which, assuming a temperature coefficient of capacitance α_c ,

(11)
$$C_{20^{\circ},p}[1 + \alpha_{c}(t - 20)] = \kappa'_{t,p} \left(C_{20,0} + \frac{\partial C_{20,0}}{\partial p} \Delta p \right) [1 + \alpha_{c}(t - 20)]$$
$$= [1 + (\kappa' - 1)_{20^{\circ},1 \text{ atm}} \cdot Q_{t,p}] \left(C_{20,0} + \frac{\partial C_{20,0}}{\partial p} \Delta p \right) [1 + \alpha_{c}(t - 20)].$$

Hence

(12)
$$(\kappa' - 1)_{20^{\circ}, 1 \text{ atm}} \approx \frac{C_{20, p} - C_{20, 0}}{Q_{t, p} \cdot C_{20, 0}} - \frac{1}{C_{20, 0}} \cdot \frac{\partial C_{20, 0}}{\partial p} \Delta p,$$

where

(13)
$$C_{20,p} = (C_{t,p})_{\mathbf{M}}[1 - \alpha_c(t-20)],$$

(14)
$$C_{20,0} = (C_{t',0})_{\mathbf{M}} [1 - \alpha_{\iota}(t' - 20)],$$

and $(C_{t,p})_{\mathbf{M}}$ and $(C_{t',0})_{\mathbf{M}}$ are the capacitances measured, at temperatures t and t', with the capacitor filled to a pressure p or evacuated to zero pressure.

PROCEDURE

The gases used were the purest available commercially in the quantities required, and are described by the supplier, Matheson of Canada Ltd., as shown in Table II. The purities were checked by Dr. F. P. Lossing of the

TABLE II Gas purity (Matheson of Canada Ltd.)

Gas	Purity	Dew point	Measured impurity
Argon	99.998%		0.003% N ₂ * 0.0007% O ₂
Carbon dioxide Nitrogen	$99.99\% \ 99.996\%$	−90° F	0.008% O _* *
Oxygen	99.6% min.	<-70° F	$0.0015\% \text{ A} < 0.01\% \text{ N}_2\dagger$

^{*}Analytical method: mass spectrometry. †Analytical method: gas chromatography.

Division of Pure Chemistry, with the results also shown in Table II. Carbon dioxide presented a problem, but no impurities of any appreciable magnitude were identified, and the supplier's data were taken to be representative of the particular cylinder of gas used. It will also be noted that the cylinder of oxygen used proved to have considerably higher purity than the minimum claimed by the supplier.

No further purification was attempted, other than to place trays of phosphorus pentoxide (P_2O_5) in the capacitor housing to absorb any water vapor which might still be present, particularly with carbon dioxide. No change in results was detectable for the data with or without the P_2O_5 and it was concluded that water vapor was not a problem with these gases.

The cross capacitor was used with the long detector bars (Dunn 1964) to provide a capacitance of approximately 1.5 pF (1 pF = 1 picofarad = 10^{-12} F). Measurements were made with the capacitor housing evacuated to a pressure less than 0.03 mm of mercury and again when filled with one of the gases to a pressure of approximately 760 mm of mercury. Alternate evacuations and refillings provide a series of capacitance values from which the relative permittivity is derived. It is to be noted that a second gas could be introduced into the evacuated housing without having to purge the capacitor to remove traces of the initial gas. This is due to the insensitivity of the capacitance configuration to adsorbed layers of a dielectric material.

The capacitance values were measured in terms of four standard 1-pF capacitors maintained at a constant temperature of $25^{\circ} \pm 0.05^{\circ}$ C which themselves are measured periodically in terms of the computable capacitor to establish their values in an absolute sense. The precision of capacitance measurements was ± 0.1 aF (1 aF = 1 attofarad = 10^{-18} F). From previous experience with the computable capacitor, no measurements were made unless the temperature differentials were less than 0.1° C, and the mean temperature

was within $\pm 0.5^{\circ}$ C of the reference temperature of 20° C. Although the tanks of gas were maintained under the same temperature conditions as the capacitor, a period of at least one hour was allowed after filling to permit the gas to come to temperature equilibrium with the housing and the capacitor. The temperature of 10 locations on the capacitor and in the housing was measured in order to determine possible temperature gradients, and to define a mean temperature of the capacitor. It is estimated that the mean temperature was self-consistent during the course of the measurements to within $\pm 0.02^{\circ}$ C.

The capacitance values measured at mean temperature t were reduced to the reference temperature of 20° C using the dilation coefficient of the steel bars forming the capacitor, which had been measured by the Interferometry Section of the Division of Applied Physics to be $+11.0 \times 10^{-6}$ per °C. As steel was the material forming the cross capacitor, the capacitance change with pressure was determined from eq. (2) to be $(1/c)\partial c/\partial p = -0.27 \times 10^{-6}$ per atmosphere, using the values $E = 19.3 \times 10^{11}$ dyne cm⁻² and $\sigma = 0.29$.

The equilibrium pressure in the capacitor housing was measured by means of a precision cathetometer and a mercury manometer of large-bore tubing. The evacuated pressures were also checked with a Pirani vacuum gauge, which helped to establish the zero correction of the manometer. The standard atmosphere is defined as a pressure of 1.013250×10^6 dyne cm⁻², which is the pressure exerted by a 760.00-mm column of mercury of density $\rho_8 = 13.5951$ g cm⁻³ at 0° C, under conditions where $g_8 = 980.665$ cm sec⁻². Under other conditions of temperature and gravitational acceleration, the observed mercury heights h must be reduced to standard conditions by the expression

$$h_{\rm s} = h \cdot \frac{\rho}{\rho_{\rm s}} \cdot \frac{g}{g_{\rm s}}.$$

Values of ρ/ρ_s were taken from Brombacher *et al.* (1960), as were the data for correcting the observed heights of mercury for the capillary depression of the mercury column. The local value of the gravitational acceleration was determined to be g = 980.615 cm sec⁻². It is estimated that the pressure data are self-consistent to approximately ± 0.05 mm mercury.

RESULTS

A series of approximately forty alternate fillings and evacuations of the computable cross-capacitor housing was made for each of the four gases used. The results of these measurements of the relative permittivities are listed in Table III. The precision of measurement and comparison has become so high

TABLE III

Relative permittivities of four gases (Frequency = 1592 c.p.s.)

Gas	$(\kappa'-1)_{20}$ °,1 atm $\times 10^6$	$(\kappa'-1)_{0}$ °,1 atm $ imes 10^{6}$	Number of measurements
Argon	516.59 ± 0.2	554.54 ± 0.2	18
Carbon dioxide Nitrogen	$921.62\pm0.3 547.40\pm0.2$	990.55 ± 0.3 587.58 ± 0.2	$\begin{array}{c} 22 \\ 26 \end{array}$
Oxygen	494.31 ± 0.2	530.61 ± 0.2	20

that the departures from the perfect gas laws as noted in Table I must be taken into account, and this has been done in the values quoted.

The limits of error in the measurements are derived as follows:

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Random error: standard deviation of experimental results reduced to 20° C and 1- atmosphere pressure \pm 0.13 \times 10^{-6}

Estimated maximum systematic errors:

(a) thermometer calibration: \pm 0.02^{\circ} C \pm 0.06 \times 10^{-6}

(b) manometer corrections (tilt of cathetometer and surface tension of mercury): \pm 0.05 mm \pm 0.07 \times 10^{-6}

(c) dilation coefficient of steel: \pm 0.05 \times 10^{-6}/° C \pm 0.05 \times 10^{-6}

(d) (1/c) \frac{\partial c}{\partial p}: \pm 0.03 \times 10^{-6}/atmosphere \pm 0.03 \times 10^{-6}

(e) C_{20,0}: <\pm 0.0005\%

SUM = \pm 0.345 \times 10^{-6}

STATISTICAL TOTAL = \pm 0.17 \times 10^{-6}
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An estimated error of $\pm 0.2 \times 10^{-6}$ has been adopted for these measurements, and this should be regarded as being equivalent to a standard deviation.

The errors due to ± 0.1 aF precision of measurement of capacitance, $\pm 0.02^{\circ}$ C in mean temperature values, and ± 0.05 mm in mercury heights are included in the experimental spread of results, and do not contribute further to the systematic errors.

From Table II, carbon dioxide is seen to be only 99.99% pure, and to account for a possible indeterminacy of 0.01% in the sample purity, wider accuracy limits have been quoted for this gas. For the other three gases, impurities of less than 0.01% have no appreciable effect on the measured values, as the impurity gases have approximately the same value of relative permittivity.

COMPARISON OF RESULTS

In Table IV these measurements are compared with the data from other experimenters. In most cases the original measurements were made at approximately room temperature and then corrected to standard conditions of 0° C and 1-atmosphere pressure. In Table IV the original data have been recorrected to reference conditions of 20° C and 1-atmosphere pressure, using the same assumptions of gas laws used by the original experimenters, in order to provide comparison data which are closer to the mean results actually obtained.

The tolerances quoted in Table IV for each listed value have been taken from the original sources. In many of the optical-dispersion extrapolations, the tolerances have been derived from examination of the final formula quoted, having regard to the fact that a least-squares adjustment was generally made in deriving the formula, which may encourage the inclusion of an extra significant figure which is only valid for interpolation between bounds, rather than extrapolation to infinite wavelength. It is estimated that the effective tolerances for the optical data in Table IV are within $\pm 50\%$ of the value derived in this manner. The refractivity data for oxygen have been corrected by means of eq. (1), assuming $\kappa'_m = 1.0000019$.

The tolerances listed explicitly in the original data are sometimes ambiguous, although generally a statistical evaluation was used and the resulting figure represents a statistical standard deviation, that is a 65% confidence level.

TABLE IV Comparison of relative permittivities of four gases at 20° C and 1-atmosphere pressure

			$(\kappa' - 1)_{20^{\circ}} _{\rm C, \ 1 \ atm} \times 10^{6}$	× 10°	
Reference	Frequency (Mc)	Argon	Carbon dioxide	Nitrogen	Oxygen
Dunn (this paper)	0.001592	516.59 ± 0.2	921.62 ± 0.3	547.40 ± 0.2	494.31 ± 0.2
Lovering (1951) Watson of all (1931)	0.1	507.8 ± 1.4 518.0 ± 1	919.7±2 919.4±2	928.0±1.4	<i>432.0</i> ±1.4
Watson et al. (1934)	4 4		921.5 ± 1	547.2 ± 1	494.3 ± 1
Hector and Woernley (1946)		507.9 ± 0.5	920.1 ± 2	540.0≠1	487.6 ± 1
Jeiaus (1946) Jasinski and Berry (1954)	3360	0.12±.010	920.57 ± 0.7	548.74±0.4	494.20±0.4
Lyons et al. (1948) Econ (1953)	0006 0006		919.2 ± 2	546.9 ± 2 548.07 ± 0.2	495.6 ± 2
Essen (1999) Birnbaum <i>et al.</i> (1951)	9280		918.3 ± 6.9	546.9 ± 4.1	493.8 ± 3.7
Zieman (1952)	9470	() ()	920.1 ± 4.1	547.0±2	495.2 ± 2
Zieman (1953) Essen and Froome (1951)	. 9700 24000	517.0 ± 1.9 516.67 ± 0.4	920.78 ± 2	548.07 ± 0.2	494.65 ± 0.4
Cuthbertson and Cuthbertson (1909)	Optical			548.9 ± 0.4	494.5 ± 0.5
Cuthbertson and Cuthbertson (1910)	Optical	516.9 ± 0.2		548 95±0 4	
Koch (1913) Cuthbertson and Cuthbertson (1920)	Optical Optical		820.9 ± 0.7	040.44 ±0.4	
Quarder (1924)	Optical	517.82 ± 0.2			8.0+77.167
Tausz and Gorlachter (1931)	Optical	517.02 ± 0.4		547.24 ± 0.4	492.9±0.4
Ladenberg and Wolfsohn (1932) Damitchler (1934)	Optical Ontical	516 7+0 5			438.01 ±0.0
Watson and Ramaswamy (1936)	Optical		815.9 ± 0.5	547.9±0.4	492.8∓0.4
		516.75 ± 0.2	920.29 ± 1.1	547.71 ± 0.6	494.19 ± 0.8

It is to be noted that the 95% confidence level, represented by twice the statistical standard deviation, frequently corresponds to the simple sum of the listed errors, both random and systematic. The tolerance figures quoted in Table IV probably lie somewhere between these two limits.

The data of some experimenters are listed in italics in Table IV, which signifies that there seems to be an unexplained systematic error in their results which places all, or most, of their data either consistently lower or higher than the accumulated mean of the other data over the years, and departs from the results obtained here by at least five times the statistical standard deviation assumed for their results.

The mean values listed in Table IV are obtained after deleting these italicized values from the list. The tolerances listed for these mean values are an average deviation from the mean value, taken without regard to sign.

The measurements of the relative permittivities, or dielectric constants, of the gases argon, nitrogen, and oxygen at this low audio frequency of 1592 c.p.s. agree remarkably well with the microwave and optical measurements. These three gases do not have an infrared vibration-rotation spectrum, i.e., their atomic polarization α_a is zero, and it is expected that the optical-refractivity data extrapolated to infinite wavelength should agree with the static relative permittivity.

On the other hand, carbon dioxide has a strong infrared vibration-rotation spectrum, i.e., a relatively large value of α_a , and it is to be expected that the extrapolated optical data would not agree with the observed low-frequency data. This is amply borne out by the values listed in Table IV.

CONCLUSIONS

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The measurements of the relative permittivities, or dielectric constants, of the gases argon, nitrogen, and oxygen by a capacitance-change method at a low audio frequency of 1592 c.p.s. agree remarkably well with the microwave and optical refractivity measurements, as expected, because their atomic polarization is zero. The measurements on carbon dioxide agree with the radio and microwave frequency results, but not with the optical data. Extrapolation of the optical data neglects the contribution to the static dielectric constant of the atomic polarization which is relatively large in carbon dioxide, as indicated by the strong infrared vibration-rotation spectrum of this gas.

A simple method of measuring relative permittivities of gases and vapors at an audio frequency has been established, with an accuracy at least as high as obtainable by other methods recorded in the literature. The values obtained may be used as reference values to permit the calibration of other types of permittivity apparatus, and hence extend the accuracy of measurements on other molecules.

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